

# FLICKERING AND THERMAL FLICKER WAVES ON CATALYTIC WIRES AND GAUZES AND IN CHEMICAL REACTORS\*

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**Abstract.** We present a theoretical investigation of flickering (local temperature fluctuations) and thermal flicker waves in chemical reactors and on catalytic wires and gauzes. It is shown that these phenomena can be caused by harmonic coupling between the chemical kinetics and oscillations in the ambient field. The oscillations can be modeled either by fluctuations in the heat and mass transfer coefficients, or by fluctuations in the gas temperature and concentration.

**1. Introduction.** Local temperature fluctuations (flickering) are observed in chemical reactors (for example, in ammonia oxidation convertors) and on catalytic wires and gauzes [1], [2]. Ervin and Luss [1] have argued that these temperature oscillations of the catalytic surface are due to the coupling between the chemical reaction and the random fluctuations of the turbulent flow past the wire. They have proposed that the coupling is effected through fluctuations in the turbulent transport coefficients. For the special case of a catalytic wire in which longitudinal conduction of heat is ignored, they present some numerical and experimental results to support this proposition. Until now no theoretical investigation has been conducted of flickering in chemical reactors or, apart from [1], on catalytic wires; moreover, no theory has been given for the more usual cases where longitudinal heat conduction is present.

We shall show that Ervin and Luss [1] may be correct, in the sense that the hypothesis of fluctuating transport coefficients can provide an explanation of flickering. On the other hand, we shall show that an alternative hypothesis, namely that the temperature and concentration in the gas phase surrounding the wire are fluctuating rather than uniform, leads eventually to the same mathematical model, and therefore provides an equally plausible explanation of flickering. We show also that either hypothesis leads to an interaction which is responsible for steady and slowly-varying thermal flicker waves. Indeed, other mechanisms such as fluctuations in the concentrations of the reacting species [8] which have been suggested as causes of flickering lead to similar mathematical problems.

In § 2 we present the governing equations and pose the problems we study. The demonstration of flickering is presented in § 3, and finally in § 4 we study the thermal flicker waves. To be specific our analysis is presented for the catalytic wire, and we shall interpret all quantities relative to this situation. However, since the mathematical equations, when longitudinal heat conduction is present, are the same as those for tubular reactors, our results apply equally well to this situation also.

**2. The catalytic wire.** Following Aris [2] we first consider the simplest situation, in which the wire is infinitely long and impermeable, but capable of conducting heat. This heat is generated by reaction on the surface which is exposed to constant ambient conditions. Aris presents the governing equations as

$$(2.1) \quad pk_c(c_f - c) = pr(c, T),$$

$$(2.2) \quad kA \frac{d^2 T}{dz^2} + ph(T_f - T) + (-\Delta H)pr(c, T) = 0,$$

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where  $p$  = perimeter of cross-section,  $A$  = area of cross-section,  $k_c$  = mass transfer coefficient,  $h$  = heat transfer coefficient,  $z$  = position on wire,  $\Delta H$  = heat of reaction,  $k$  = conductivity of wire,  $c(z)$  = concentration on the wire,  $T(z)$  = temperature on the wire,  $c_f$  = ambient concentration,  $T_f$  = ambient temperature, and  $r(c, T)$  = reaction rate function. The standard non-dimensionalization of these equations is accomplished by setting

$$u = \frac{c}{c_f}, \quad v = \frac{T}{T_f}, \quad F(u, v) = \frac{r(c, T)}{r(c_f, T_f)}, \quad \nu = \frac{k_c c_f}{r(c_f, T_f)},$$

$$\mu = \frac{h T_f}{(-\Delta H) r(c_f, T_f)}, \quad x = z \left[ \frac{(-\Delta H) p r(c_f, T_f)}{k A} \right]^{1/2}.$$

Then (2.1)–(2.2) become

$$(2.3) \quad \nu(1 - u) = F(u, v),$$

$$(2.4) \quad \frac{d^2 v}{dx^2} + \mu(1 - v) + F(u, v) = 0.$$

To study time-dependent phenomena such as flickering and flicker waves we shall need the time-dependent (or transient) equations, which are

$$(2.5) \quad \frac{\partial u}{\partial t} = \nu(1 - u) - F(u, v),$$

$$(2.6) \quad L \frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2} + \mu(1 - v) + F(u, v),$$

where the heat capacity parameter is given by

$$L = \frac{C_p A T_f}{(-\Delta H) p c_f}.$$

Here  $C_p$  is the heat capacity per unit volume. We have assumed that the wire is so fine that radial gradients are unimportant. We shall consider  $n$ -order Arrhenius kinetics. Thus

$$(2.7) \quad F(u, v) = P_n(u) e^{-\gamma/v},$$

where  $P_n(u)$  is an  $n$ th degree polynomial in the concentration  $u$ , and  $\gamma$  = dimensionless activation energy ( $E/RT$ ).

We now relax our assumption that the wire is exposed to constant ambient conditions. First of all, following Ervin and Luss [1], we assume that turbulent flow past the wire affects the wire through instantaneous changes in the heat and mass transfer coefficients  $h$  and  $k_c$ . The velocity fluctuations should be represented by a complete spectrum of frequencies. However, as was originally suggested by Lighthill [3], a simple model to study the theoretical effect of coupling these fluctuations to the chemical kinetics can be obtained by assuming that all fluctuations have the same frequency, and that these fluctuations are small perturbations on a constant free stream flow. Thus we take the mass and heat transfer coefficients to be

$$k_c(1 + \alpha_1 \sin \omega_0 t), \quad 0 < \alpha_1 < 1,$$

$$h(1 + \alpha_2 \sin \omega_0 t), \quad 0 < \alpha_2 < 1,$$

respectively. Therefore, the governing equations (2.5) and (2.6) become

$$(2.8) \quad \frac{\partial u}{\partial t} = \nu(1 + \varepsilon\beta_1 \sin \omega_0 t)(1 - u) - F(u, v),$$

$$(2.9) \quad L \frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2} + \mu(1 + \varepsilon\beta_2 \sin \omega_0 t)(1 - v) + F(u, v),$$

with  $0 < \varepsilon < 1$ .

These equations are based on the hypothesis that the ambient gas temperature and concentration are constant. An alternative model can be obtained by assuming that these quantities fluctuate sinusoidally, while the heat and mass transfer coefficients are constant. In this model we take the ambient concentration and temperature to be of the form

$$c_f(1 + \alpha_1 \sin \omega_0 t), \quad 0 < \alpha_1 < 1,$$

$$T_f(1 + \alpha_2 \sin \omega_0 t), \quad 0 < \alpha_2 < 1,$$

respectively. Then (2.5)–(2.6) become

$$(2.10) \quad \frac{\partial u}{\partial t} = \nu(1 + \varepsilon\beta_1 \sin \omega_0 t - u) - F(u, v),$$

$$(2.11) \quad L \frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2} + \mu(1 + \varepsilon\beta_2 \sin \omega_0 t - v) + F(u, v).$$

The systems (2.8)–(2.9) and (2.10)–(2.11) are similar, but not quite identical. They can be combined in the form

$$(2.12) \quad \frac{\partial u}{\partial t} = \nu[1 - u + \varepsilon\beta_1(1 - \lambda u) \sin \omega_0 t] - F(u, v),$$

$$(2.13) \quad L \frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2} + \mu[1 - v + \varepsilon\beta_2(1 + \lambda v) \sin \omega_0 t] + F(u, v),$$

where  $\lambda = 1$  in the case (2.8)–(2.9) and  $\lambda = 0$  in the case (2.10)–(2.11).

Finally, we note that in tubular reactors in which diffusive terms in the concentration are important and which often operate nonadiabatically, the governing equations would become

$$(2.14) \quad \frac{\partial u}{\partial t} = D_1 \frac{\partial^2 u}{\partial x^2} + \nu[1 - u + \varepsilon\beta_1(1 - \lambda u) \sin \omega_0 t] - F(u, v),$$

$$(2.15) \quad L \frac{\partial v}{\partial t} = D_2 \frac{\partial^2 v}{\partial x^2} + \mu[1 - v + \varepsilon\beta_2(1 - \lambda v) \sin \omega_0 t] + F(u, v).$$

Although our main goal is to account for the observations of flickering on catalytic wires and to predict other related phenomena, our results are true for the more general situations described by equations (2.14)–(2.15).

**3. Flickering.** We shall consider the full system (2.14)–(2.15) of partial differential equations in § 4. First, however, we examine the simplified situation for the catalytic wire in which longitudinal conduction of heat is ignored or, equivalently, where

solutions independent of  $x$  are sought. Thus we study

$$(3.1) \quad \frac{du}{dt} = \nu[1 - u + \varepsilon\beta_1(1 - \lambda u) \sin \omega_0 t] - F(u, v),$$

$$(3.2) \quad L \frac{dv}{dt} = \mu[1 - v + \varepsilon\beta_2(1 - \lambda v) \sin \omega_0 t] + F(u, v).$$

For the case of constant ambient conditions ( $\varepsilon = 0$ ) with the first-order Arrhenius kinetics ( $F(u, v) = ue^{-\gamma/v}$ ), Ervin and Luss [1] have shown that (3.1)–(3.2) possesses three steady-state solutions for a certain range of the ambient gas temperature  $T_f$ , which is proportional to both the Lewis number  $L$  and the dimensionless heat transfer coefficient  $\mu$ . Furthermore, they have shown that the high temperature steady state, denoted by  $(U, V)$ , is stable at very large gas temperature  $T_f$  by virtue of two real negative eigenvalues of the linear stability matrix. Decreasing  $T_f$  induces complex conjugate eigenvalues with negative real parts; with further decrease in  $T_f$ , the real parts of the eigenvalues become positive and the state  $(U, V)$  loses its stability.

Ervin and Luss [1] have taken into account the effect of fluctuations in the case  $\lambda = 1$  and  $\beta_1 = \beta_2$ . They perform numerical integrations of (3.1)–(3.2) at parameter values where the eigenvalues of the stability matrix are complex conjugates with negative real parts. They find an oscillatory response (i.e., flickering) of resonance type when  $\omega_0$  is near the imaginary part of the stability eigenvalues. On the basis of their computations they conclude that their conjecture is correct.

We now extend Ervin and Luss's study analytically in order to isolate and identify the features and parameters controlling the coupling between the chemical kinetics and the fluctuating ambient conditions. We shall confirm Ervin and Luss's results on the maximum response at the resonant frequency when the stability eigenvalues have negative real parts. In addition, however, we shall demonstrate a far more dramatic effect when the real parts of the stability eigenvalues tend to zero.

We transform (3.1)–(3.2) by moving the origin of  $(u, v)$  to the high temperature steady state solution  $(U, V)$ . Thus we set

$$u \rightarrow U + u, \quad v \rightarrow V + v,$$

whereupon (3.1)–(3.2) take the form

$$(3.3) \quad \frac{du}{dt} = (-\nu - F_u)u - F_v \cdot v + \varepsilon\nu\beta_1(1 - \lambda U) \sin \omega_0 t - \varepsilon\nu\beta_1\lambda \cdot u \sin \omega_0 t - G(u, v),$$

$$(3.4) \quad L \frac{dv}{dt} = F_u \cdot u + (-\mu + F_v)v + \varepsilon\mu\beta_2(1 - \lambda V) \sin \omega_0 t - \varepsilon\mu\beta_2\lambda \cdot v \sin \omega_0 t + G(u, v),$$

where  $F_u F_v$  denote the partial derivatives of  $F$  with respect to  $u, v$  evaluated at  $(U, V)$ , and where  $G = O(u^2 + v^2)$ . A simple linear transformation enables (3.3)–(3.4) to be replaced by

$$(3.5) \quad \frac{du}{dt} = \gamma u - \omega v + \varepsilon\delta_1 \sin \omega_0 t + \varepsilon\gamma(\rho_{11}u + \rho_{12}v) \sin \omega_0 t + f(u, v),$$

$$(3.6) \quad \frac{dv}{dt} = \omega u + \gamma v + \varepsilon\delta_2 \sin \omega_0 t + \varepsilon\gamma(\rho_{21}u + \rho_{22}v) \sin \omega_0 t + g(u, v).$$

Here the  $\delta_i$  are constants depending on  $\lambda$  which do not in general vanish when either  $\lambda = 0$  or  $\lambda = 1$ ; the  $\rho_{ij}$  are constants depending on  $\mu, \nu$  and  $\beta_i$  but not on  $\lambda$ ; and we have

explicitly isolated the eigenvalues  $\gamma \pm i\omega$  of the linearized stability matrix. The functions  $f$  and  $g$  are  $O(u^2 + v^2)$ ; in fact, for first-order Arrhenius kinetics it is easily shown that

$$f = \alpha_{11}uv + \alpha_{12}v^2 + O[(u^2 + v^2)^{3/2}], \quad g = \alpha_{21}uv + \alpha_{22}v^2 + O[(u^2 + v^2)^{3/2}],$$

where the  $\alpha_{ij}$  are constants. The procedure for solving (3.5)–(3.6) is by a standard multiple scaling perturbation technique. As is well known, the slow scale is determined by the leading order resonant interaction which is necessarily cubic since quadratic nonlinearities cannot interact resonantly. In other words, it is the cubic, not the quadratic nonlinearities which yield the desired behavior of the system in the neighborhood of a bifurcation point. Therefore, we suppress the quadratic nonlinearities, and for algebraic simplicity we consider in place of (3.5)–(3.6) the system

$$(3.7) \quad \frac{du}{dt} = \gamma u - \omega v + \varepsilon \delta_1 \sin \omega_0 t + \varepsilon \gamma u \sin \omega_0 t - 2u^3,$$

$$(3.8) \quad \frac{dv}{dt} = \omega u + \gamma v + \varepsilon \delta_2 \sin \omega_0 t + \varepsilon \lambda v \sin \omega_0 t - 2u^2 v.$$

This is the simplest model which reveals the desired underlying structure of the general problem, namely the resonant interaction between the cubic terms and the imposed oscillation.

When  $\gamma = O(1)$  as  $\varepsilon \rightarrow 0$ , the system (3.7)–(3.8) has a periodic solution which can be determined as a regular perturbation in powers of  $\varepsilon$ :

$$(3.9) \quad u(t) = \varepsilon u_0(t) + \varepsilon^2 u_1(t) + \cdots, \quad v(t) = \varepsilon v_0(t) + \varepsilon^2 v_1(t) + \cdots.$$

The equations for the leading terms are

$$(3.10) \quad \frac{du_0}{dt} = \gamma u_0 - \omega v_0 + \delta_1 \sin \omega_0 t, \quad \frac{dv_0}{dt} = \omega u_0 + \gamma v_0 + \delta_2 \sin \omega_0 t;$$

the solution of this system is easily obtained, and we refrain from giving the details. However, for the purposes of comparison with Ervin and Luss [1], we note that in the case  $\gamma < 0$  and with transients neglected, the amplitudes of the responses are found to be

$$(3.11) \quad |u_0| = \left\{ \frac{(\delta_1 \omega_0)^2 + (\delta_1 \gamma + \delta_2 \omega)^2}{(\gamma^2 + \omega^2 - \omega_0^2)^2 + 4\gamma^2 \omega_0^2} \right\}^{1/2},$$

$$(3.12) \quad |v_0| = \left\{ \frac{(\delta_2 \omega_0)^2 + (\delta_2 \gamma + \delta_1 \omega)^2}{(\gamma^2 + \omega^2 - \omega_0^2)^2 + 4\gamma^2 \omega_0^2} \right\}^{1/2}.$$

The value of  $\omega_0$  at which these attain their maximum values can be computed when the other parameters are specified. It is obvious, however, that the value at which these maxima occur approaches  $\omega$  as  $\gamma \rightarrow 0$ ; this agrees with the numerical result of Ervin and Luss.

As  $\gamma$  increases through zero the solution (3.9) becomes unstable and bifurcation into a stable modulated limit cycle occurs. When  $\varepsilon = 0$  the limit cycle has the form

$$u(t) = U_0(t), \quad v(t) = V_0(t),$$

where  $U_0, V_0$  are periodic functions with period  $T = 2\pi/\omega[1 + o(\gamma^2)]$  when  $\gamma$  is small. For  $\varepsilon \neq 0$  the solution is modified into the form

$$u(t) = U_0(t) + \varepsilon U_1(t) + \cdots, \quad v(t) = V_0(t) + \varepsilon V_1(t) + \cdots$$

and is quasiperiodic with periods  $T$  and  $T_0 = 2\pi/\omega_0$ . This regular perturbation breaks down at resonance ( $\omega = \omega_0$ ) when  $\gamma \rightarrow 0$ .

The limit  $\gamma \rightarrow 0$  is singular because the denominators in (3.11)–(3.12) become unbounded at the resonance value  $\omega = \omega_0$ . To study the behavior of the system near resonance as  $\gamma \rightarrow 0$ , we need to perform a suitable rescaling. We set

$$(3.13) \quad \omega_0 = \omega + \alpha \varepsilon^{2/3}, \quad \gamma = \sigma \varepsilon^{2/3},$$

and employ a standard multi-scale perturbation procedure. Thus we let

$$(3.14) \quad u(t) = u(t^*, \tau) = \varepsilon^{1/3} u_0(t^*, \tau) + \varepsilon^{2/3} u_1(t^*, \tau) + \varepsilon u_2(t^*, \tau) + \cdots,$$

$$(3.15) \quad v(t) = v(t^*, \tau) = \varepsilon^{1/3} v_0(t^*, \tau) + \varepsilon^{2/3} v_1(t^*, \tau) + \varepsilon v_2(t^*, \tau) + \cdots,$$

where

$$(3.16) \quad t^* = (\omega + \alpha \varepsilon^{2/3})t, \quad \tau = \varepsilon^{2/3}t,$$

and we seek bounded functions  $u_i(t^*, \tau)$ ,  $v_i(t^*, \tau)$ ,  $i = 0, 1, 2, \dots$ . Then

$$\frac{d}{dt} = (\omega + \alpha \varepsilon^{2/3}) \frac{\partial}{\partial t^*} + \varepsilon^{2/3} \frac{\partial}{\partial \tau}.$$

Upon inserting (3.13)–(3.16) into (3.7)–(3.8) and equating coefficients of like powers of  $\varepsilon$ , we obtain

$$(3.17) \quad \omega \frac{\partial u_0}{\partial t^*} + \omega v_0 = 0, \quad \omega \frac{\partial v_0}{\partial t^*} - \omega u_0 = 0,$$

$$(3.18) \quad \omega \frac{\partial u_1}{\partial t^*} + \omega v_1 = 0, \quad \omega \frac{\partial v_1}{\partial t^*} - \omega u_1 = 0,$$

$$(3.19) \quad \omega \frac{\partial u_2}{\partial t^*} + \omega v_2 = -\alpha \frac{\partial u_0}{\partial t^*} - \frac{\partial u_0}{\partial \tau} + \sigma u_0 - 2u_0^3 + \delta_1 \sin t^*,$$

$$(3.20) \quad \omega \frac{\partial v_2}{\partial t^*} - \omega u_2 = -\alpha \frac{\partial v_0}{\partial t^*} - \frac{\partial v_0}{\partial \tau} + \sigma v_0 - 2u_0^2 v_0 + \delta_2 \sin t^*.$$

The solution of (3.17) is

$$(3.21) \quad u_0(t^*, \tau) = R(\tau) \cos(t^* + \phi(\tau)),$$

$$(3.22) \quad v_0(t^*, \tau) = R(\tau) \sin(t^* + \phi(\tau)),$$

where the unknown functions  $R(\tau)$  and  $\phi(\tau)$  will be determined at a later stage of the perturbation procedure. Similarly, the solution of (3.18) is

$$(3.23) \quad u_1(t^*, \tau) = S(\tau) \cos(t^* + \psi(\tau)),$$

$$(3.24) \quad v_1(t^*, \tau) = S(\tau) \sin(t^* + \psi(\tau)).$$

Using (3.21)–(3.22) we find that (3.19)–(3.20) become

$$(3.25) \quad \omega \frac{\partial u_2}{\partial t^*} + \omega v_2 = (-R' + \sigma R - \frac{3}{2}R^3) \cos(t^* + \phi) \\ + (R\phi' + \alpha R) \sin(t^* + \phi) + \delta_1 \sin t^* + \text{other harmonics},$$

$$(3.26) \quad \omega \frac{\partial v_2}{\partial t^*} - \omega u_2 = (-R\phi' - \alpha R) \cos(t^* + \phi) \\ + (-R' + \sigma R - \frac{1}{2}R^3) \sin(t^* + \phi) + \delta_2 \sin t^* + \text{other harmonics}.$$

The right-hand sides of (3.25)–(3.26) come from expanding the right-hand sides of (3.19)–(3.20) in Fourier series, or alternatively, by simply employing trigonometrical identities. We have retained only those harmonics which correspond to forcing at resonance; these terms must be eliminated or they will produce unbounded solutions  $u_1$  and  $v_1$ . The elimination is achieved by applying the Fredholm alternative (see Cohen [4]) and leads to the following two conditions:

$$(3.27) \quad (R' - \sigma R + R^3) \sin \phi + (R\phi' + \alpha R) \cos \phi + \frac{1}{2}\delta_1 = 0,$$

$$(3.28) \quad (R' - \sigma R + R^3) \cos \phi - (R\phi' + \alpha R) \sin \phi - \frac{1}{2}\delta_2 = 0.$$

These can be rearranged to read

$$(3.29) \quad \frac{dR}{d\tau} = \sigma R - R^3 - \beta \sin \theta,$$

$$(3.30) \quad R \frac{d\theta}{d\tau} = -\alpha R - \beta \cos \theta,$$

where

$$(3.31) \quad \beta = \frac{1}{2}\sqrt{\delta_1^2 + \delta_2^2}, \quad \theta = \phi - \arctan(\delta_2/\delta_1).$$

Therefore to leading order in  $\varepsilon$  the solution of (3.7)–(3.8) is given by (3.14)–(3.15), where the evolution equations for the amplitude  $R(\tau)$  and the phase  $\phi(\tau)$  are given by (3.29)–(3.30).

We examine the nature of the solutions of (3.29)–(3.30). To begin with we consider the special case  $\alpha = 0$  which corresponds to exact resonance between the natural frequency  $\omega$  and the forcing frequency  $\omega_0$ , and therefore represents the worst case of failure of the regular perturbation.

When  $\alpha = 0$  the equilibrium solutions of (3.29)–(3.30) are obviously given by

$$(3.32) \quad F(R) \equiv R^3 - \sigma R - \beta = 0, \quad \theta = \frac{3\pi}{2},$$

and

$$(3.33) \quad G(R) \equiv R^3 - \sigma R + \beta = 0, \quad \theta = \frac{\pi}{2}.$$

Since  $F(R) \rightarrow \pm\infty$  as  $R \rightarrow \pm\infty$ , and since  $F(0) = -\beta < 0$ , it is clear that (3.32) always has at least one real positive root,  $R$ , say, for all values of  $\sigma$ . Moreover,  $F(R)$  has no extrema when  $\sigma < 0$ , and has extrema at  $R = \pm\sigma/\sqrt{3}$  when  $\sigma > 0$ . In the latter case the maximum is at the negative value of  $R$  and the minimum at the positive value. From these observations we conclude that  $R_1$  is the *unique positive* real root of (3.32).

Similarly, (3.33) always has one negative real root (which is unphysical), and has either no positive root or two positive roots. The transition occurs when

$$(3.34) \quad G(R) = 0, \quad G'(R) = 0$$

hold simultaneously. A simple calculation shows that, in terms of the parameter  $\sigma$ , this transition is identified by  $\sigma = \sigma_c$ , where  $\sigma_c$  is given by

$$(3.35) \quad \sigma_c^3 = \frac{27\beta^2}{4}.$$

Equation (3.33) is easily seen to have two real roots  $R_2$  and  $R_3$  when  $\sigma > \sigma_c$  and no real root when  $\sigma < \sigma_c$ .

Combining these results we see that (3.29)–(3.30) with  $\alpha = 0$  have three equilibrium solutions when  $\sigma > \sigma_c$ , and one solution when  $\sigma < \sigma_c$ . In particular there is only one solution when  $\sigma = 0$ .

To determine the stability of these solutions we set

$$(3.36) \quad R = \bar{R} + \rho, \quad \theta = \bar{\theta} + \eta$$

in (3.29)–(3.30), where  $\bar{R}$  denotes any of the solutions  $R_1, R_2, R_3$ , and  $\bar{\theta}$  the corresponding values  $3\pi/2$  or  $\pi/2$ . Linearizing the equations we obtain

$$(3.37) \quad \begin{pmatrix} \frac{d\rho}{d\tau} \\ \frac{d\eta}{d\tau} \end{pmatrix} = \begin{pmatrix} \sigma - 3\bar{R}^2 & -\beta \cos \bar{\theta} \\ \frac{\beta}{\bar{R}} \cos \bar{\theta} & \frac{\beta}{\bar{R}} \sin \bar{\theta} \end{pmatrix} \begin{pmatrix} \rho \\ \eta \end{pmatrix},$$

or upon using the critical point relationships,

$$(3.38) \quad \begin{pmatrix} \frac{d\rho}{d\tau} \\ \frac{d\eta}{d\tau} \end{pmatrix} = \begin{pmatrix} \sigma - 3\bar{R}^2 & \alpha \bar{R} \\ \frac{-\alpha}{\bar{R}} & \sigma - \bar{R}^2 \end{pmatrix} \begin{pmatrix} \rho \\ \eta \end{pmatrix}.$$

It is now easy to establish that the solution  $R_1$  is always stable, while  $R_2$  and  $R_3$ , when they exist, are both unstable. Figures 1 and 2 illustrate the character of these solutions.

To summarize, we see that as  $\sigma$  (or  $\gamma$ ) increases towards zero through negative values the regular perturbation solution (3.9) is replaced by the multi-scale solution (3.14)–(3.15) at resonance. It is important to note that the response to the ambient fluctuations is  $O(\varepsilon)$  when  $\gamma$  is not close to zero, but increases to  $O(\varepsilon^{1/3})$  at resonance when  $\gamma \rightarrow 0$ ; this is relatively a very large response.

As  $\gamma$  increases through zero, ( $\sigma > 0$ ), solutions of the form (3.14)–(3.15) persist and eventually merge with the modulated null solution and modulated limit cycles described above. A detailed account of how these mergings are effected will be given in [5].

Finally we note that the structure of the solutions is the same when  $\lambda = 0$  or  $\lambda = 1$ . This means that the flickering can be explained in terms of either variable transport coefficients or variable ambient temperature and concentration.

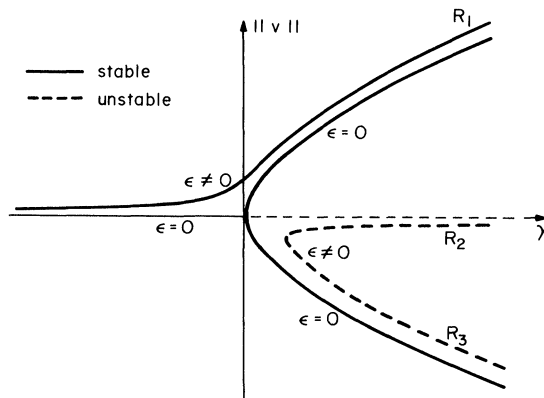


FIG. 1



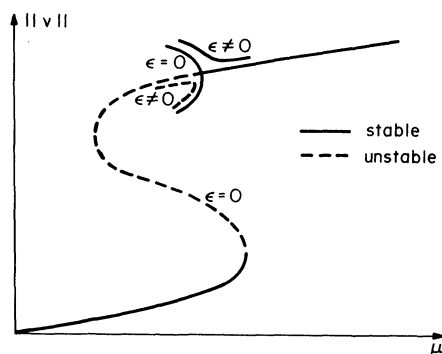


FIG. 2

Qualitatively similar results are obtained when  $\alpha \neq 0$ , but the analysis is more formidable. When  $\alpha \neq 0$  the equilibrium solutions of (3.29)–(3.30) are given by

$$(3.39) \quad R^3 - \sigma R + \beta \sin \theta = 0, \quad \alpha R + \beta \cos \theta = 0,$$

which can be combined to give the single equation

$$H(R) \equiv R^6 - 2\sigma R^4 + (\sigma^2 + \alpha^2)R^2 - \beta^2 = 0.$$

Equation (3.40) has at least one real positive root  $R_1$  for all  $\sigma$ ; this follows since  $H(R) \rightarrow \infty$  as  $R \rightarrow \pm\infty$  and  $H(0) = -\beta^2 < 0$ . Now  $H(R)$  always has a minimum at  $R = 0$ ; its other extrema are given by

$$R^2 = \frac{\sigma}{3} \{2 \pm \sqrt{1 - 3\alpha^2/\sigma^2}\}.$$

Hence there are no extrema when  $\sigma < \sqrt{3}\alpha$ , so that when this inequality holds there is only one positive root  $R_1$ . Actually, new positive roots first appear at the value  $\sigma_c$  of  $\sigma$  for which  $H(R) = 0$ ,  $H'(R) = 0$  hold simultaneously. The determination of  $\sigma_c$  requires the numerical solution of a sixth degree polynomial. We shall not perform this calculation since the qualitative behavior is similar to that for the case  $\alpha = 0$ .

**4. Thermal flicker waves.** We now consider the full system (2.14)–(2.15) of partial differential equations. For the catalytic wire this amounts to recognizing that longitudinal conduction of heat occurs realistically; for tubular reactors it amounts to recognizing that diffusive effects are always present and that long tubular reactors are not stirred tanks in which we can ignore diffusion. Again, for algebraic simplicity and for ease of presentation, we consider the specific nonlinearities of equations (3.7)–(3.8). Thus we study

$$(4.1) \quad \frac{\partial u}{\partial t} = \gamma u - \omega v + \varepsilon \delta_1 \sin \omega_0 t + \varepsilon \lambda u \sin \omega_0 t - 2u^3 + D_1 \frac{\partial^2 u}{\partial x^2},$$

$$(4.2) \quad \frac{\partial v}{\partial t} = \omega u + \gamma v + \varepsilon \delta_2 \sin \omega_0 t + \varepsilon \lambda v \sin \omega_0 t - 2u^2 v + D_2 \frac{\partial^2 v}{\partial x^2}.$$

For catalytic wires  $D_1 = 0$ , while for reactors both diffusion coefficients are nonzero.

First, we note that the solutions of § 3 are also solutions of (4.1)–(4.2). We shall now show that if these solutions are subjected to spatially dependent perturbations, the effect of the diffusive terms in (4.1)–(4.2) is to modulate these solutions in the form of slowly progressing waves. More precisely we shall show that the system (4.1)–(4.2)

possesses solutions of the form  $R(\xi + c\tau)P(t^*)$ , where  $P(t^*)$  represents oscillations (flickering) on a fast time scale  $t^*$ , and  $R(\xi - c\tau)$  represents a slowly modulating amplitude on slow space  $\xi$  and slow time  $\tau$  scales. In the absence of diffusion this reduces to the solutions  $R(\tau)P(t^*)$  found in § 3.

Our analysis follows that of Cohen, Hoppensteadt and Miura [6] who studied slowly modulated oscillations as bifurcations in nonlinear diffusion processes represented by autonomous reaction-diffusion equations. Certain suitable modifications must be made to account for the nonautonomous nature of the present problem and the different scalings which are required; but the procedure is then the same. Thus we invoke the scaling (3.13), and we let

$$(4.3) \quad u(x, t) = u(\xi, t^*, \tau) = \varepsilon^{1/3} u_0(\xi, t^*, \tau) + \varepsilon^{2/3} u_1(\xi, t^*, \tau) + \varepsilon u_2(\xi, t^*, \tau) + \cdots,$$

$$(4.4) \quad v(x, t) = v(\xi, t^*, \tau) = \varepsilon^{1/3} v_0(\xi, t^*, \tau) + \varepsilon^{2/3} v_1(\xi, t^*, \tau) + \varepsilon v_2(\xi, t^*, \tau) + \cdots,$$

where

$$(4.5) \quad \xi = \varepsilon^{1/3} x, \quad \tau = \varepsilon^{2/3} t, \quad t^* = (\omega + \alpha \varepsilon^{2/3}) t.$$

Upon carrying out the perturbation analysis just as in § 3, we obtain

$$(4.6) \quad u_0(\xi, t^*, \tau) = R(\xi, \tau) \cos(t^* + \phi(\xi, \tau)),$$

$$(4.7) \quad v_0(\xi, t^*, \tau) = R(\xi, \tau) \sin(t^* + \phi(\xi, \tau)),$$

where

$$(4.8) \quad \frac{\partial R}{\partial \tau} = D \left[ \frac{\partial^2 R}{\partial \xi^2} - R \left( \frac{\partial \theta}{\partial \xi} \right)^2 \right] + \sigma R - R^3 - \beta \sin \theta,$$

$$(4.9) \quad R \frac{\partial \theta}{\partial \tau} = D \left[ R \frac{\partial^2 \theta}{\partial \xi^2} + 2 \frac{\partial R}{\partial \xi} \frac{\partial \theta}{\partial \xi} \right] - \alpha R - \beta \cos \theta,$$

with

$$(4.10) \quad D = \frac{1}{2}(D_1 + D_2), \quad \beta = \frac{1}{2}\sqrt{\delta_1^2 + \delta_2^2}, \quad \theta = \phi - \arctan(\delta_2/\delta_1).$$

The equations (4.8)–(4.9) are clearly the generalizations to partial differential equations of the evolution equations (3.29)–(3.30) of § 3. Many types of solutions of systems like (4.8)–(4.9) exist; see [6], [7]. Here, in order to account for thermal flicker waves, we shall look for traveling wave solutions. Thus we let  $\eta = \xi - c\tau$  and look for solutions of the form

$$(4.11) \quad R(\xi, \tau) = R(\xi - c\tau) \equiv R(\eta),$$

$$(4.12) \quad \theta(\xi, \tau) = \theta(\xi - c\tau) \equiv \theta(\eta).$$

Then (4.8)–(4.9) become

$$(4.13) \quad D[R'' - R(\theta')^2] + cR' + \sigma R - R^3 - \beta \sin \theta = 0,$$

$$(4.14) \quad D[R\theta'' + 2R'\theta'] + cR' - \alpha R - \beta \cos \theta = 0.$$

Just as in § 3, we focus attention on the special case  $\alpha = 0$  corresponding to exact resonance between the natural frequency  $\omega$  and the forcing frequency  $\omega_0$ . Qualitatively similar solutions can be obtained for the case  $\alpha \neq 0$ , but the analysis is much more complex. With  $\alpha = 0$  we write (4.14) in the form

$$(4.15) \quad (R^2 e^{\delta\eta} \theta')' = \frac{\beta}{D} R e^{\delta\eta} \cos \theta, \quad \delta = \frac{c}{D}.$$

Thus,

$$(4.16) \quad R^2(\eta)\theta'(\eta) = K e^{-\delta\eta} + \frac{\beta}{D} e^{-\delta\eta} \int_0^\eta R(\eta) e^{\delta\eta} \cos \theta(\eta) d\eta.$$

With the requirement that  $R(\eta)$  be bounded for all  $\eta \in (-\infty, \infty)$ , the exponential growth for  $\theta'(\eta)$  as  $\eta \rightarrow \infty$  or  $-\infty$  implied by (4.16) destroys consistency at higher orders in the perturbation procedure [6]. To overcome this, we take  $K = 0$  and  $\cos \theta(\eta) = 0$ , so that  $\theta'(\eta) = 0$ . Note that  $\cos \theta(\eta) = 0$  expresses the same requirement on  $\theta$  as was needed in § 3 with  $\alpha = 0$  (i.e., equations (3.32)–(3.33)). Thus we have  $\theta(\eta) = \bar{\theta}$ , where  $\bar{\theta} = \pi/2$  or  $\bar{\theta} = 3\pi/2$ .

When  $\theta(\eta) = \bar{\theta} = \text{constant}$ , (4.13) becomes

$$(4.17) \quad DR'' + cR + \sigma R - R^3 - \beta \sin \bar{\theta} = 0.$$

We show now that this equation possesses a stable periodic solution which has the form of a limit cycle in the  $R - R'$  plane. We note first that (4.17) has the critical points  $\bar{R} = R_1, R_2, R_3$  defined in § 3, with  $R_1$  associated with  $\bar{\theta} = 3\pi/2$  and  $R_2, R_3$  with  $\bar{\theta} = \pi/2$ . Setting

$$(4.18) \quad R(\eta) = \bar{R} + r(\eta),$$

in (4.17), we obtain the equation

$$(4.19) \quad Dr'' + cr' + \Omega r - (3\bar{R}r^2 + r^3) = 0,$$

where  $\Omega = \Omega(\bar{R})$  is defined by equation (3.38). Now, as shown in § 3,  $\Omega < 0$  when  $\bar{R} = R_1$  and when  $\bar{R} = R_3$ . Hence the critical points  $R_1$  and  $R_3$  are saddle points. On the other hand  $\Omega > 0$  when  $\bar{R} = R_2$ , and this corresponds to a spiral point when  $c^2 < 4\Omega$ . In this case there is a possibility of a limit cycle around this critical point. In fact we can be sure that there is a stable limit cycle for a range of wave speeds  $c$ ; for when  $|c|$  is small enough it can be used as a small parameter to develop a limit cycle solution by standard multi-scale or Poincaré-Lindstedt type perturbation procedures.

Therefore, the system (4.13)–(4.14) possesses the stable limit cycle  $\theta(\eta) = \pi/2$ ,  $R(\eta) = R_2 + r(\eta)$ , and thus we have established the existence of thermal flicker waves

$$(4.20) \quad u \sim R(\varepsilon^{1/3}x + c\varepsilon^{2/3}t) \cos \left( \omega t + \frac{\pi}{2} - \arctan \frac{\delta_2}{\delta_1} \right),$$

$$(4.21) \quad v \sim R(\varepsilon^{1/3}x - c\varepsilon^{2/3}t) \sin \left( \omega t + \frac{\pi}{2} - \arctan \frac{\delta_2}{\delta_1} \right),$$

where the modulating envelope represents a periodic traveling wave.

In conclusion, we recall the remark above that the solutions of § 3, which have no spatial structure, are also solutions of the diffusive system (4.1)–(4.2). This means that the latter system has three stable solutions—the space-independent ones represented by  $R_1$  and  $R_3$ , and the traveling wave solution (4.20)–(4.21)—all of which are modulations about the unstable mean  $R_2$ . Initial conditions will presumably determine onto which of these a disturbance evolves.

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